Diffusion of Multicomponent Solids
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Lecture 44

Last class we talked about interdiffusion analysis in binary systems. Today, we will study interdiffusion analysis in multi component systems.

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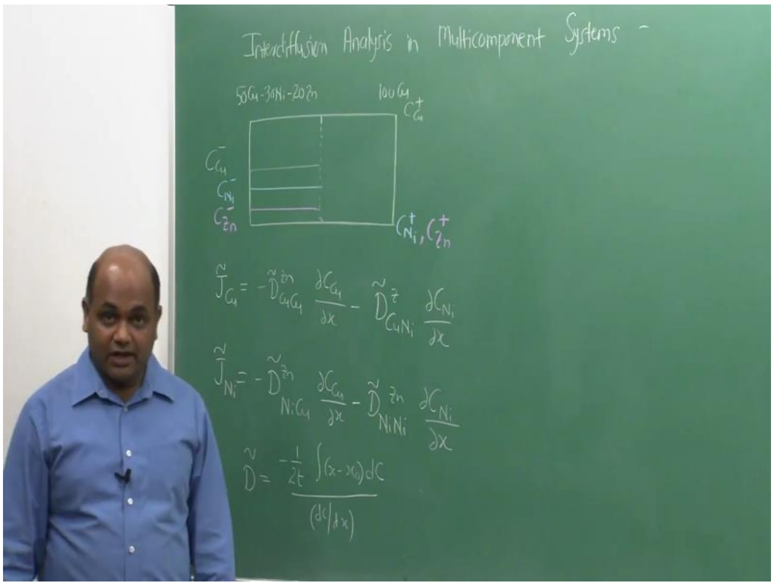

For example, let us consider a ternary diffusion couple. Let us say on left side, we have an alloy, 50 copper-30 nickel-20 zinc. Right side we have pure copper, that is 100% copper. The left terminal alloy concentration of copper is C^-_{Cu}. Right side concentration would be C^+_{Cu}. We also have $C^+_{Ni} = 0$, $C^+_{Zn} = 0$ in the right terminal alloy.

Since, we are dealing with ternary diffusion couple, we have two independent fluxes. If we take zinc as dependent component, we can write for copper:

$$\tilde{J}_{Cu} = -\tilde{D}^{Zn}_{CuCu}\frac{\partial C_{Cu}}{\partial x} - \tilde{D}^{Zn}_{CuNi}\frac{\partial C_{Ni}}{\partial x}$$

Foe nickel it will be:

$$\tilde{J}_{Ni} = -\tilde{D}^{Zn}_{NiCu}\frac{\partial C_{Cu}}{\partial x} - \tilde{D}^{Zn}_{NiNi}\frac{\partial C_{Ni}}{\partial x}$$

So, we need four interdiffusion coefficients at any given composition of the ternary systems.

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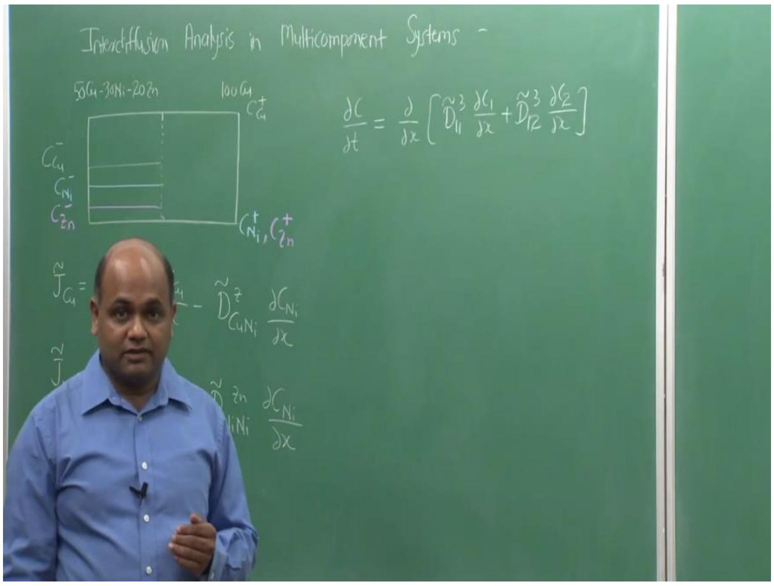

How do we find this? For binary, we used the formula:

$$\widetilde{D} = \frac{-1}{2t\left(\frac{\partial C}{\partial x}\right)} \int_{C^-}^{C_{(x)}} (x - x_o)dC$$

If you compare with Fick’s law, this straight away tells me that the numerator is nothing but the interdiffusion flux. But this we can say for binary system. How do we go about finding interdiffusion coefficients in ternary? Because if we apply the continuity equation, it is not as simple as for binary as now it is a coupled equation.

If you consider in general components 1-2-3 you can write the continuity equation as:

$$\frac{\partial C_1}{\partial t} = \frac{\partial}{\partial x}\left[\widetilde{D}_{11}^{3}\frac{\partial C_1}{\partial x} + \widetilde{D}_{12}^{3}\frac{\partial C_2}{\partial x}\right]$$

In order to go ahead, we will use a very powerful approach which was proposed by Dayananda. With this approach we first find out the interdiffusion flux directly from the concentration profile that develops in the diffusion couple at the end of the diffusion annealing.

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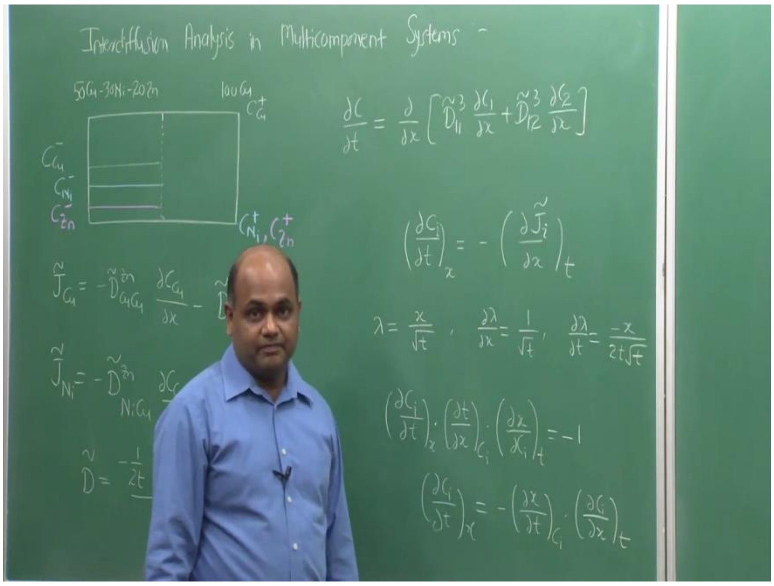

Let us see how do we go about this? We know the continuity equation:

$$\left(\frac{\partial C}{\partial t}\right)_x = -\left(\frac{\partial \tilde{J}}{\partial x}\right)_t$$

For ternary, we have two independent concentration variables. So, we need to mention at least two concentrations in order to completely define a composition. So, we would like to denote the flux and concentration with subscript i:

$$\left(\frac{\partial C_i}{\partial t}\right)_x = -\left(\frac{\partial \tilde{J}_i}{\partial x}\right)_t$$

Again, we would like to use the Boltzmann parameter, λ which is:

$$\lambda = \frac{x}{\sqrt{t}}$$

We assume that each composition plane that develops in a multi component diffusion zone is also a function of λ. This has been shown to be true in many of the ternary diffusion couples experimentally. Then we have:

$$\frac{\partial\lambda}{\partial x} = \frac{1}{\sqrt{t}} \quad , \quad \frac{\partial\lambda}{\partial t} = -\frac{x}{2t\sqrt{t}}$$

If you look at the left hand side, in the thermodynamics refresher, we had seen the upstairs, downstairs inside-out formula for the partial derivatives, which we can apply here. We can write with that formula:

$$\left(\frac{\partial C_i}{\partial t}\right)_x \left(\frac{\partial t}{\partial x}\right)_{C_i} \left(\frac{\partial x}{\partial C_i}\right)_t = -1$$

We get:

$$\left(\frac{\partial C_i}{\partial t}\right)_x = -\left(\frac{\partial x}{\partial t}\right)_{C_i} \left(\frac{\partial C_i}{\partial x}\right)_t$$

Now if you look at the first term on the right hand side, $\left(\frac{\partial x}{\partial t}\right)_{C_i}$ is nothing but the velocity of the composition plane C_i.

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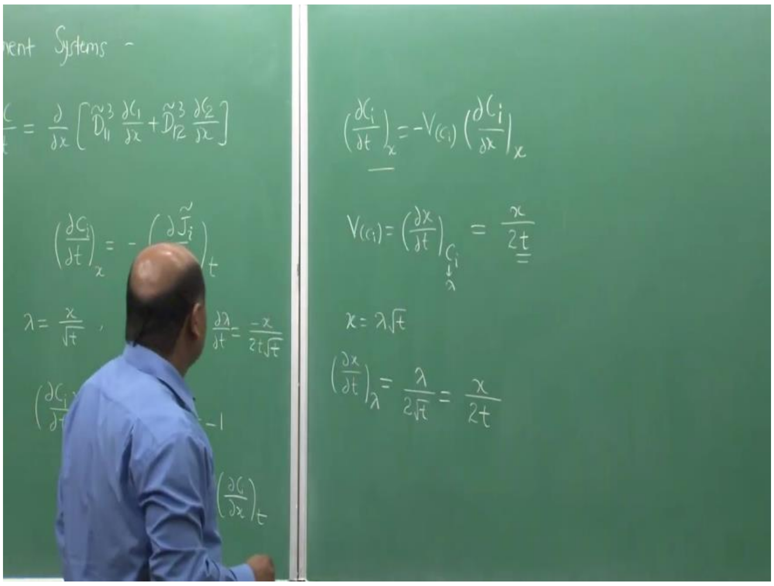

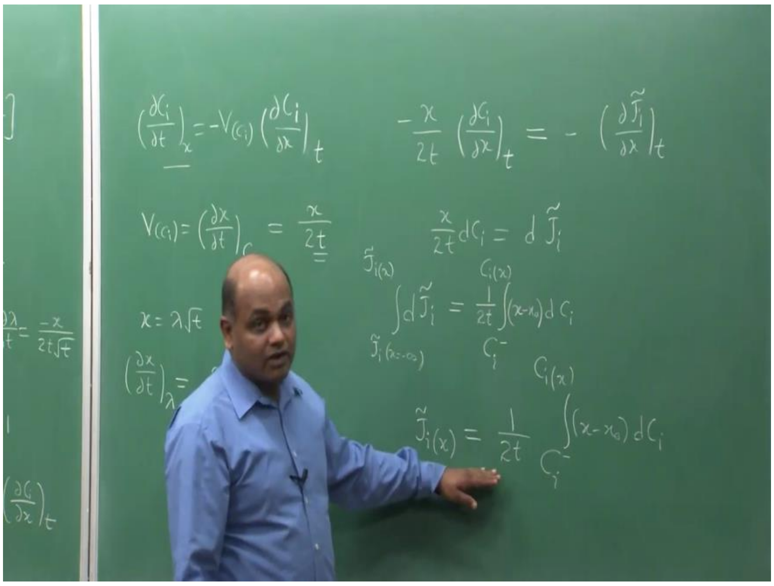

We can write:

$$\left(\frac{\partial C_i}{\partial t}\right)_x = -V_{(C_i)}\left(\frac{\partial C_i}{\partial x}\right)_t \qquad (1)$$

Now, let us try to find out this $V_{(C_i)}$:

$$V_{(C_i)} = \left(\frac{\partial x}{\partial t}\right)_{C_i}$$

Since C_i is a function of λ, we can write this as

$$V_{(C_i)} = \left(\frac{\partial x}{\partial t}\right)_{\lambda}$$

Now, we can write:

$$x = \lambda\sqrt{t}$$

Since λ is constant, we get:

$$\left(\frac{\partial x}{\partial t}\right)_{\lambda} = \frac{\lambda}{2\sqrt{t}}$$

If we substitute again for λ, this is nothing but:

$$\left(\frac{\partial x}{\partial t}\right)_{\lambda} = \frac{\lambda}{2\sqrt{t}} = \frac{x}{2t}$$

So,

$$V_{(C_i)} = \left(\frac{\partial x}{\partial t}\right)_{C_i} = \frac{x}{2t}$$

If x not is our origin, we can write it as $\frac{x-x_o}{2t}$. If we substitute back into equation (1) here then we get:

$$\left(\frac{\partial C_i}{\partial t}\right)_x = -\frac{x}{2t}\left(\frac{\partial C_i}{\partial x}\right)_t$$

Left side should be equal to $-\left(\frac{\partial \tilde{J}_i}{\partial x}\right)_t$:

$$-\left(\frac{\partial \tilde{J}_i}{\partial x}\right)_t = -\frac{x}{2t}\left(\frac{\partial C_i}{\partial x}\right)_t$$

Since the partial derivatives on both sides are at constant time, we can take those out. If we multiply both sides by dx, we get:

$$\frac{x}{2t} dC_i = d\tilde{J}_i$$

Now, if we integrate both sides from the left terminal to the desired x, we get:

$$\int_{\tilde{J}_i(x=-\infty)}^{\tilde{J}_i(x)} d\tilde{J}_i = \frac{1}{2t} \int_{C_i^-}^{C_{i(x)}} (x - x_o) dC_i$$

Here we use x_o as our reference plane. We know that the diffusants will never penetrate on the two terminals, so the fluxes at the two terminals would be 0. Or:

$$\tilde{J}_i(x = -\infty) = 0$$

We straight away get:

$$\tilde{J}_i(x) = \frac{1}{2t} \int_{C_i^-}^{C_{i(x)}} (x - x_o) dC_i \qquad (2)$$

This is how we can get formula for interdiffusion flux. So, we can obtain interdiffusion flux directly from the experimental concentration profile.

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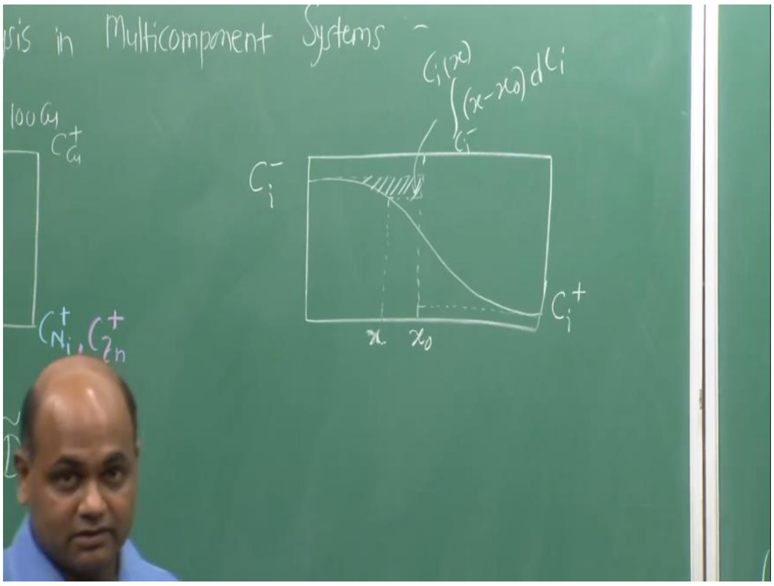

I will illustrate how. Consider any one of the profiles that developed after the diffusion annealing, let us say component i. C_i^- is again left terminal alloy concentrations, C_i^+ is the right terminal alloy concentration. If we want to evaluate the interdiffusion flux at any position x, we use the above formula. Here integral in Eq. (2) is nothing but again the area under the curve shown by shaded lines.

Matano plane x_o is shown in the figure. So, just by finding the area under the curve and dividing it by $2t$ we can get the flux at any position x. We derived this formula Eq. (2) again independent of the number of composition. So, this should be applicable to a multi component diffusion couple. This way we can obtain the interdiffusion flux of each component at every composition plane that is developed within the diffusion zone here.

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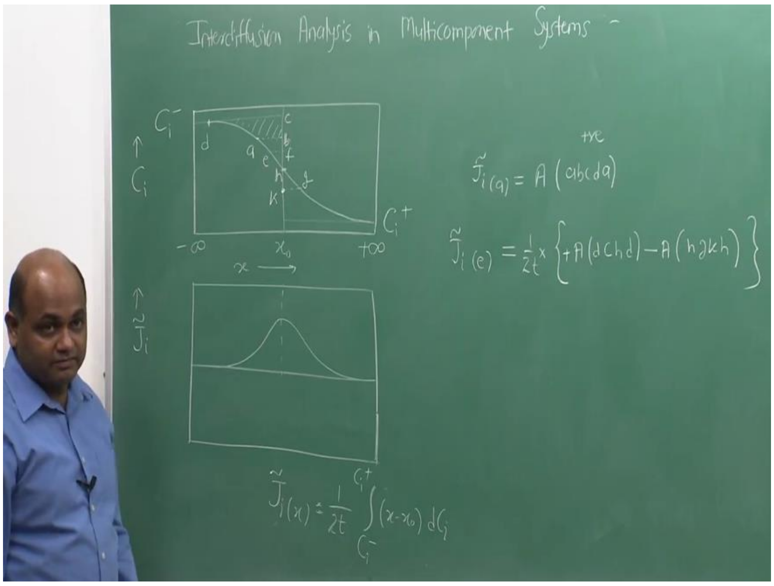

Now, let us try to look at the nature of the diffusion flux profiles that can be obtained. Consider again, this concentration profile of component i which is developed in the diffusion zone after the diffusion annealing time t. We want to determine the interdiffusion flux and we want to see the nature of diffusion flux profile in the diffusion zone.

We derived the formula for J as:

$$\tilde{J}_i(x) = \frac{1}{2t}\int_{C_i^-}^{C_{i(x)}} (x - x_o)dC_i$$

If we consider any location, let us say a here the flux will be $\frac{1}{2t}$ times the shaded area under the curve. So, this will be the area that we need to determine. Let us call this area a, b, c, d here. Let us determine sign of the flux: since $(x - x_o)$ on left side is negative, C_i is decreasing with x, so dC_i would be negative and the sign of the flux would be positive. he flux at a would be positive.

So, we know $\tilde{J}_i$ at a would be area, abcda and this would be positive. If we determine flux on the left side of matano plane but at a different location, let us say e here. Then we need to consider this area $defc$ which is again positive and greater than the area $abcd$. So, the interdiffusion flux will be higher at point e than at a. Now, the interdiffusion flux is positive and it is increasing with x until we reach this position of Matano plane.

$$\tilde{J}_i(a) = A(abcda)$$

$$\tilde{J}_i(e) = \frac{1}{2t}\{A(dchd) - A(hgkh)\}$$

What happens beyond x_o? If we consider any position, let us call this as g here, then for this, we first need to integrate up to x_o the area would be dhc. The first integral would be dhc which is positive. Next the integral from x_o to point g, that would be area hgk. First area has a positive sign but beyond x_o, $(x - x_o)$ is now positive but dC_i is still negative. So, second area will have a negative sign attached with it. As a result, the flux starts decreasing until in the right terminal, it will again reach 0.

So, this is how the interdiffusion flux profile will look in the diffusion zone. At the two terminal ends, the fluxes would be 0. That is because we are dealing with infinite diffusion couples. The infinite boundary conditions are maintained. Flux will have a maximum at the Matano plane location. Similarly, if we are dealing with a concentration profile which has opposite gradient, a positive gradient, logically the interdiffusion flux will be negative. With the similar logic we can show there will be a minimum in the interdiffusion flux at the Matano plane location.

Now this is when we are considering the normal concentration profile like this. But in multi-component systems, many times there will be maximum/minimum developed on the concentration profiles.

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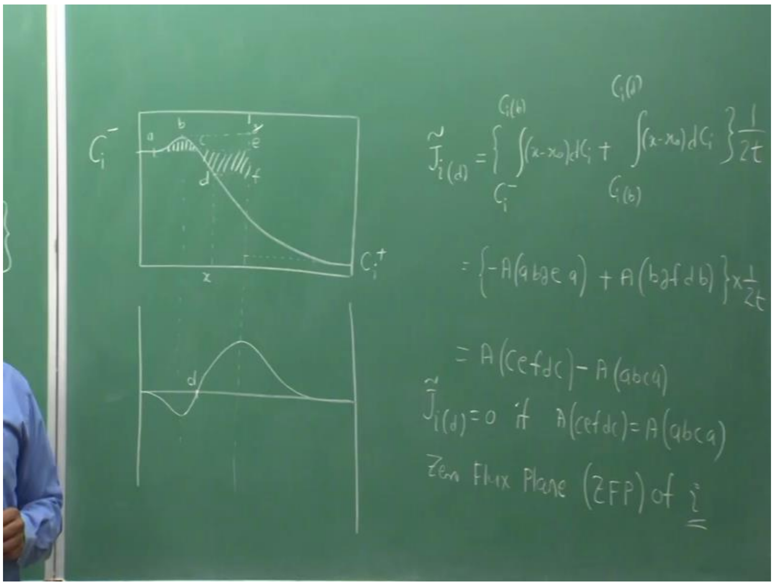

$$\tilde{J}_{i(d)} = \left\{ \int_{C_i^-}^{C_{i(b)}} (x-x_o)\,dC_i + \int_{C_{i(b)}}^{C_{i(d)}} (x-x_o)\,dC_i \right\} \frac{1}{2t}$$

$$= \left\{ -A(abgea) + A(bgfdb) \right\} \times \frac{1}{2t}$$

$$= A(cefdc) - A(abca)$$

$$\tilde{J}_{i(d)} = 0 \text{ if } A(cefdc) = A(abca)$$

Zero Flux Plane (ZFP) of i

How do we get the interdiffusion fluxes in that case, what special features it develops, let us try to look at it. Let us consider another concentration profile as shown here, there is a maximum developed on this concentration profile here. What would be the nature of interdiffusion flux profile here? Let us try to assess that. Up to the point of maximum, that is up to point b here, we know, the interdiffusion flux would be negative. Because based on the flux formula, $(x - x_o)$ is negative but dC_i from a to b is positive.

In the terminal of course the flux is 0, it is increasing in the negative direction to point b. What happens at point b? Beyond point b, now the slope of the profile has changed. Here, dC_i becomes negative, so any additional area contribution would be positive. The magnitude of flux will start decreasing beyond point b or beyond the maximum on this profile here.

If you want to find the flux at a point d for example, that we can find as:

$$\tilde{J}_i(d) = \frac{1}{2t}\left\{ \int_{C_i^-}^{C_{i(b)}} (x - x_o)dC_i + \int_{C_{i(b)}}^{C_{i(d)}} (x - x_o)dC_i \right\}$$

by splitting the integral at the point of maximum. Now, the first integral here is nothing but this area $abgea$ and it has a negative value. Second integral will be the area $bgfdb$ it will have a positive value.

$$\tilde{J}_i(d) = \frac{1}{2t}\left\{ \int_{C_i^-}^{C_{i(b)}} (x - x_o)dC_i + \int_{C_{i(b)}}^{C_{i(d)}} (x - x_o)dC_i \right\} = \frac{1}{2t}\{-A(abgea) + A(bgfdb)\}$$

There is a common area between the above two areas, $bgec$ that will get cancelled. So, we have:

$$\tilde{J}_i(d) = A(cefdc) - A(abca)$$

Since this two have different signs, we see that after maximum, the interdiffusion flux starts decreasing in magnitude here. What if the two areas are equal? :

$$\tilde{J}_i(d) = 0 \quad if \quad A(cefdc) = A(abca)$$

The flux at point d here would be 0. Beyond this point d, the magnitude of the positive area would increase, so the flux will become positive. It will keep increasing in the positive direction until the Matano plane position. Beyond Matano plane position again, the flux will start decreasing until it become 0 in the terminals. This is an interesting profile, it has a special feature in the interdiffusion flux profile. You can see, in this particular case, the flux is actually going to 0 within the diffusion zone this is called zero-flux plane (ZFP) for component i. The ZFPs are special features because they indicate that there exist strong diffusional interactions. The existence of ZFP in the flux profile of a component in a multi-component diffusion couple indicate that there are strong diffusional interactions or strong cross effects. This is also apparent form the development of uphill diffusion region here.

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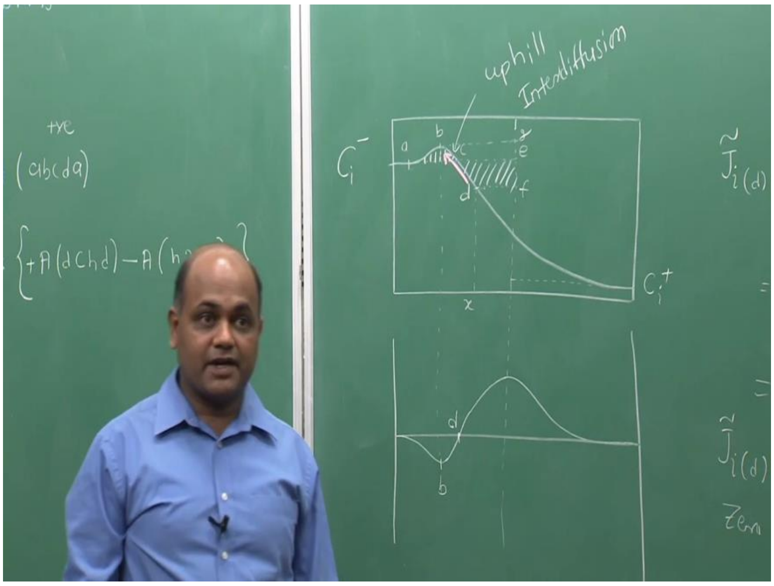

For example, from point $b\, to\, d$, you can see the flux is negative. That means in our convention, the component i is diffusing from right to left. If you see between $d\, to\, b$, the component is actually moving up its concentration gradient. This is the uphill interdiffusion region developed for component i. This is again because of the strong diffusional interactions that can occur.

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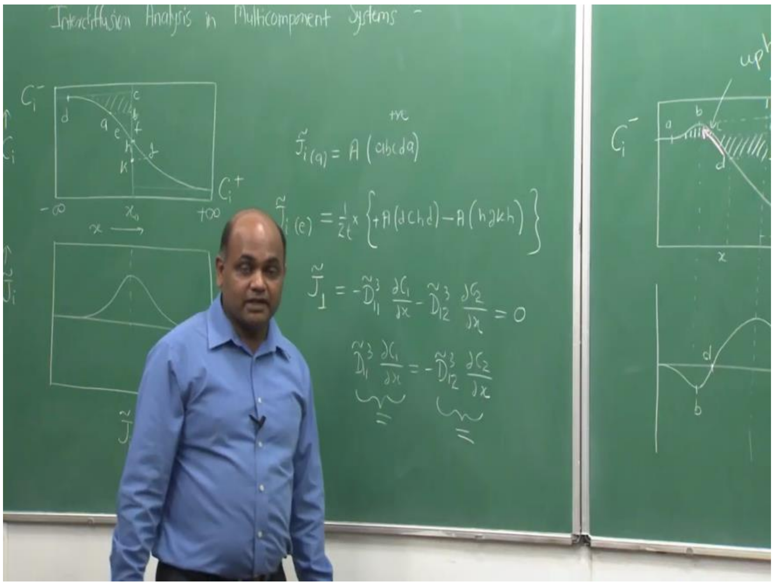

Let us see how. We know for the component 1, the interdiffusion flux is zero:

$$\tilde{J}_1 = -\tilde{D}_{11}^3 \frac{\partial C_1}{\partial x} - \tilde{D}_{12}^3 \frac{\partial C_2}{\partial x} = 0$$

Then we have:

$$\tilde{D}_{11}^3 \frac{\partial C_1}{\partial x} = -\tilde{D}_{12}^3 \frac{\partial C_2}{\partial x}$$

Which means the main term is equal to the cross term. This term characterises the effect of component 2 on the diffusion flux of 1. The first term characterises the effect of component 1 on its own diffusion flux. At the zero-flux plane, both the effects are same. That means strong diffusional interactions exist in this region. In fact in a region, the component one is moving up its own gradient, which means the effect of cross term is more than the main term. This is the significance of zero flux planes and uphill diffusion region.

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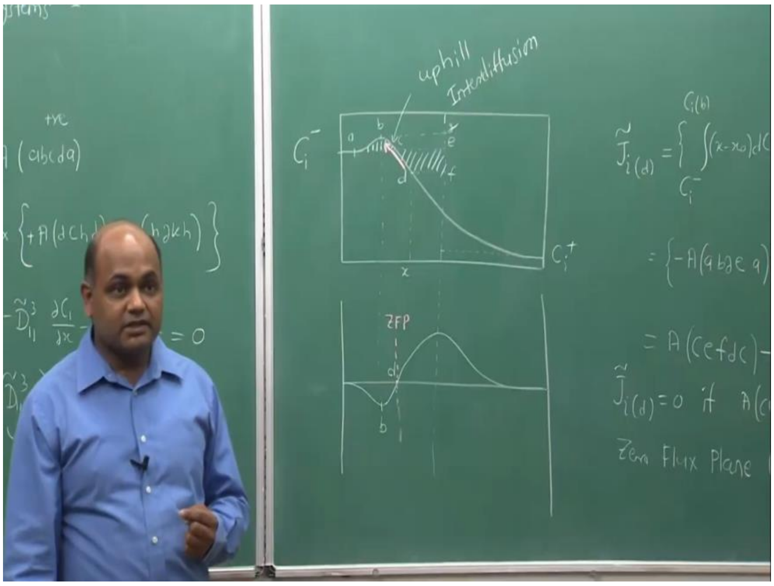

We can also see, on left side of ZFP, diffusion flux is negative. That is component is moving from right to left. On the right side, diffusion flux is positive that is the component is moving from left to right. So, there is a reversal of flux on either side of the zero-flux plane or ZFP. Also we know each composition plane is moving with time. Right? We derived the expression for velocity of composition plane earlier:

$$V_{(C_i)} = \frac{x}{2t}$$

Each composition plane is moving with time. So, zero-flux plane is also moving with time. What happens, as the zero-flux plane composition is moving, we can see in the volume swept by the ZFP, there is a continuous reversal of the flux. Where initially the flux was negative, after certain time it will become positive. So, the component is changing direction of diffusion in the volume swept by the ZFP. The ZFPs are also very important when we are studying the diffusional interactions. We want the diffusion couples which should develop ZFPs uphill diffusion regions.

Dayananda has studied such couples extensively by forming, isoactivity couples, that means a diffusion couple in which the thermodynamic activity of a component is same in both the terminal alloys to start with. In such couples the zero-flux planes are developed at a composition where the thermodynamic activity of that component is same as that in the two terminal alloys. This is how the nature of interdiffusion flux profiles look like.

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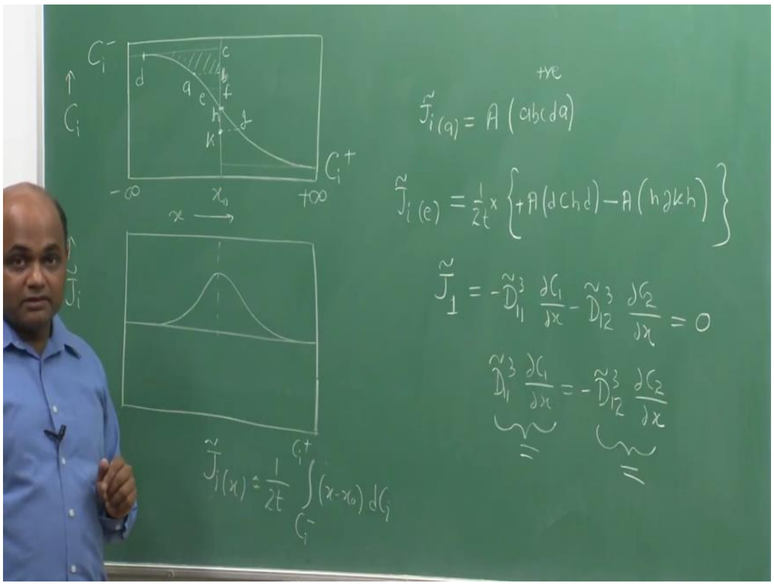

I will talk about this formula again. So far, we integrated for the interdiffusion flux from left terminal alloys. Why not from right terminal alloys? In fact, we can integrate from any of the terminal, left or right, it should not matter. I will demonstrate how.

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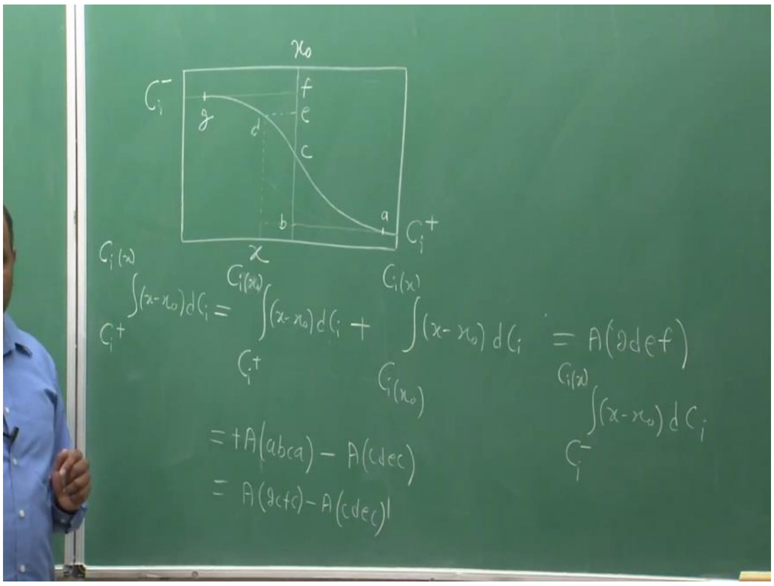

Again, consider this concentration profile, C_i^- concentration left terminal alloy, C_i^+ concentration in the right terminal alloy. Suppose if you want to determine flux at point x. If we integrate from right, instead of left, what happens? We can write:

$$\int_{C_i^+}^{C_{i(x)}} (x - x_o)\, dC_i$$

By splitting this integral at the matano plane or the initial contact plane here. We can write:

$$\int_{C_i^+}^{C_{i(x)}} (x - x_o)dC_i = \int_{C_i^+}^{C_{i(x_o)}} (x - x_o)dC_i + \int_{C_{i(x_o)}}^{C_{i(x)}} (x - x_o)dC_i = A(gdef)$$

Now, this integral is nothing but:

$$= A(abca) - A(cdec)$$

As we are integrating from right dC_i is positive because as going from right to left, C_i is increasing $(x - x_o)$ is also positive on the right side of the matano plane, so integral this has a positive sign. For second integral, $(x - x_o)$ has changed its sign because it is now negative on the left side of the matano plane, but dC_i is still positive. So, second integral has a negative sign. The way we found matano plane, we know:

$$A(abca) - A(gcfg)$$

We can write $gdef$ as:

$$A(gdef) = A(gcfc) - A(cdec)$$

Area gdef is nothing but:

$$A(gdef) = \int_{C_i^-}^{C_{i(x)}} (x - x_o)dC_i$$

So, whether you integrate from left terminal or from right terminal, it should not matter.

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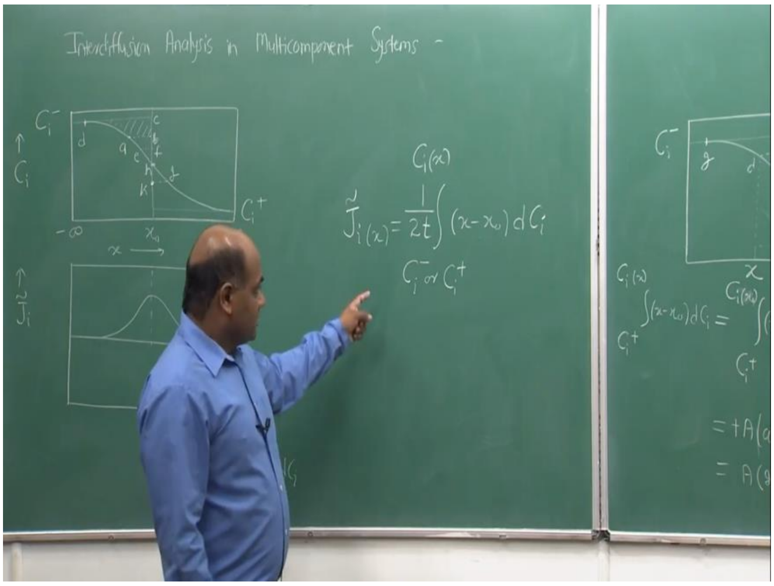

We can modify the formula little bit for $\tilde{J}_i(x)$ as:

$$\tilde{J}_i(x) = \frac{1}{2t} \int_{C_i^- \ or \ C_i^+}^{C_{i(x)}} (x - x_o) dC_i$$

Now, once we find the interdiffusion flux, our next objective is to find the interdiffusion coefficients. What is the method used for that, we will see in the next class.